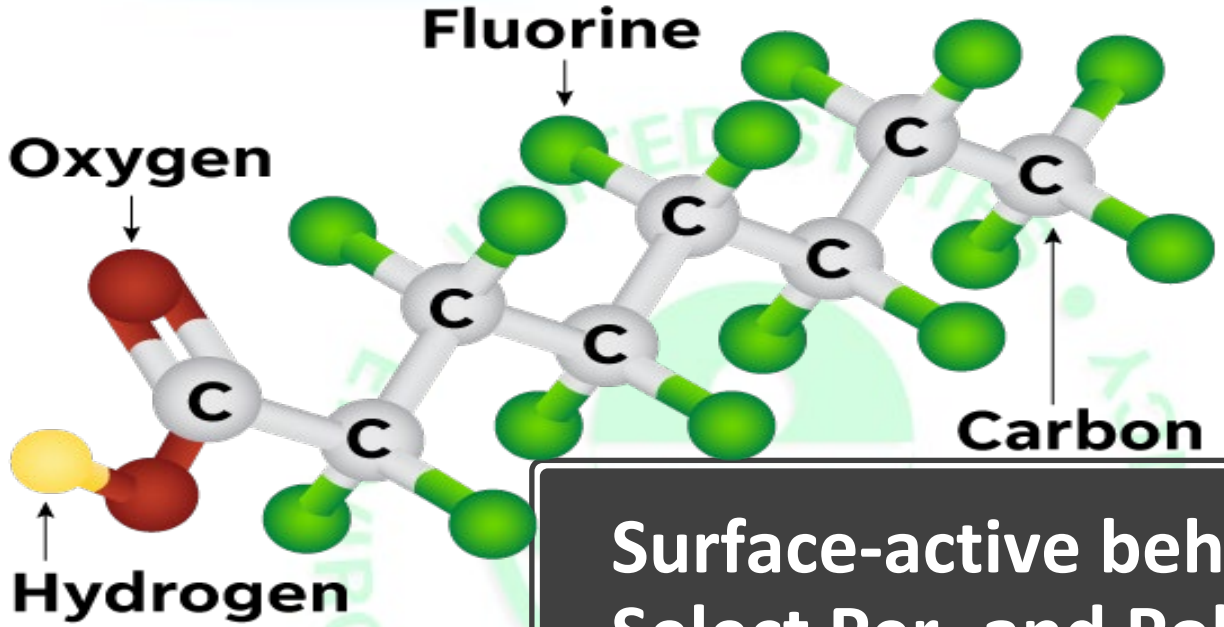



(PFOA: $C_8HF_{15}O_2$)

# Surface-active behavior of Select Per- and Polyfluoroalkyl Substances (PFAS) and their Mixtures

Jingjing Chen, Aderonke Adegbule, Junqi Huang, and Michael C. Brooks

❖ Unique properties:

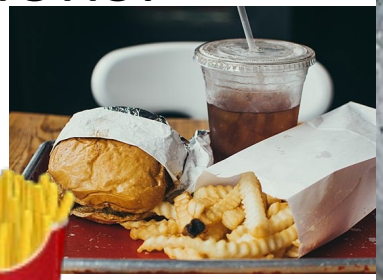
*"Permanent chemicals"*

- Strong C-F bond → Thermal + chemical stability
- Low surface energy and weak intermolecular interaction → Hydrophobic and lipophobic surfactant properties
- Strong acidity

Hydrophilic
Water-loving

Hydrophobic and lipophobic
Water and oil repellent

❖ Widespread applications:



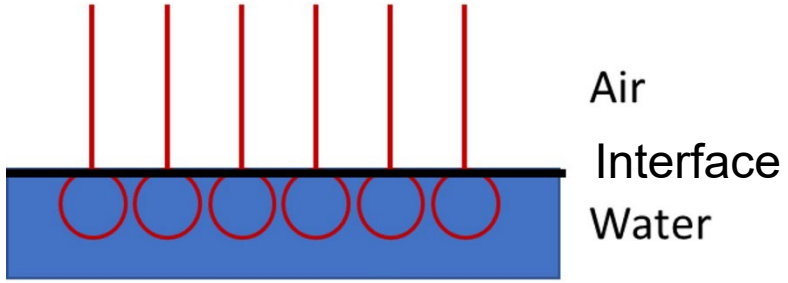
# ❖ Widely present in the environment:

- PFASs with highest concentrations and detection frequencies in the subsurface environment

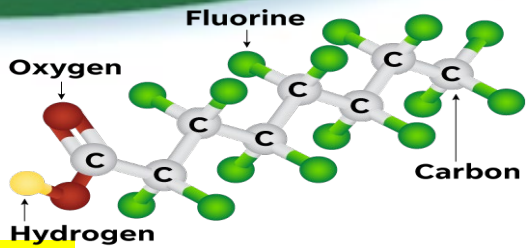
- The key to understanding the environmental fate and transport of PFAS is their surface-active behavior

Hydrophilic
Water-loving

Hydrophobic and lipophobic
Water and oil repellent

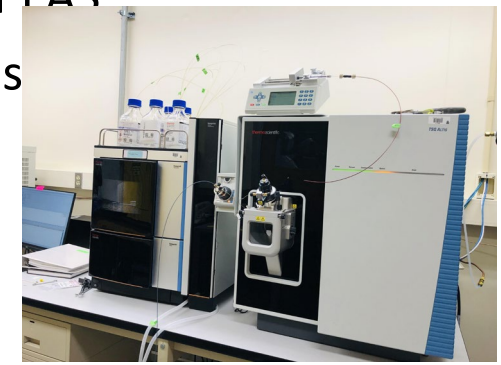


# Gaps:




## Surface-active behavior:

- Short-chain vs long-chain PFAS
- Different functional groups ($COO^-$ vs $SO_3^-$)
- Individual compounds vs Mixture



Triple Quadrupole Mass Spectrometer, Thermo scientific - TSQ Altis™

## PFAS detection:

- High cost (money and energy)
- High technology (require experts)
- Long time
- Complex pretreatments

# Questions:

- What are the surface-active characteristics of shorter-chain PFAS and mixed PFAS?
- Are there screening-level tools that may simplify PFAS contaminant characterization?

# Selected PFAS:

| PFASs | -[$CF_2$]$_n$- chain length, # of C | CAS Number | Functional groups |
|---|---|---|---|
| PFOA | n = 8, C8 | 335-67-1 | $COO^-$ |
| PFOS-K | n = 8, C8 | 2795-39-3 | $SO_3^-$ |
| PFHxA | n = 6, C6 | 307-24-4 | $COO^-$ |
| PFHxS-K | n = 6, C6 | 3871-99-6 | $SO_3^-$ |
| PFBA | n = 4, C4 | 375-22-4 | $COO^-$ |
| PFBS | n = 4, C4 | 375-73-5 | $SO_3^-$ |
| GenX | n = 4, C6 (branched) | 13252-13-6 | $COO^-$ |
| PFDA[2] | n = 10, C10 | 335-76-2 | $COO^-$ |

[2]Secondary priority.

# PFAS Mixtures

Different functional groups, but the same carbon chain length

- PFOA & PFOS-K
- PFHxS-K & PFHxA
- PFBS & GenX
- PFBA & PFBS

Different carbon chain length, but the same functional groups

- PFOA & PFBA
- PFOA & PFHxA
- PFOA & GenX
- PFOA & PFBA & PFHxA
- PFOA & PFBA & PFHxA & GenX
- PFOS-K & PFHxS-K
- PFOS-K & PFBS
- PFOS-K & PFHxS-K & PFBS

Two compounds with the highest and lowest measured surface tension

- PFOS-K & PFBA

All seven PFAS contaminants

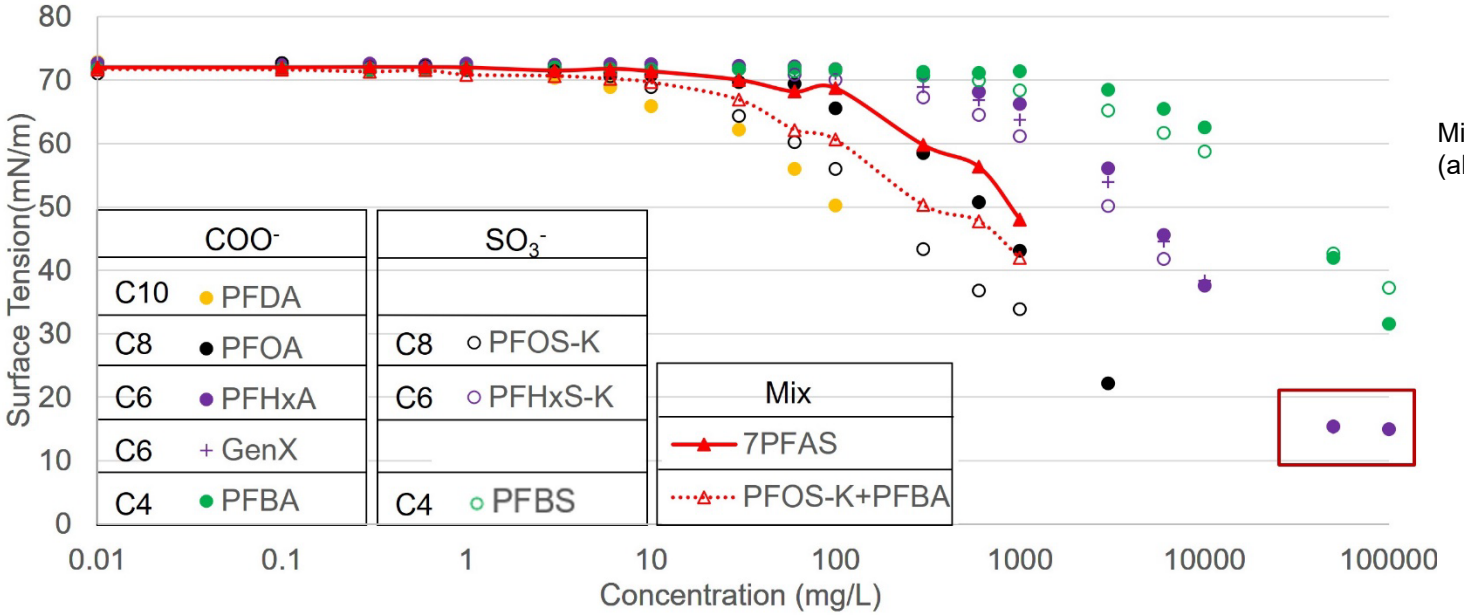
# Measurements:

- Surface tension
- pH
- Specific conductance

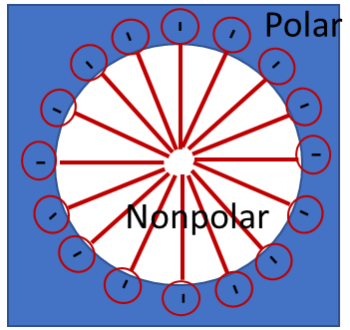

Optical tensiometer, KRUSS-DSA25


pH/Conductivity Meter, ORION-STAR A215

# Results: Surface tension

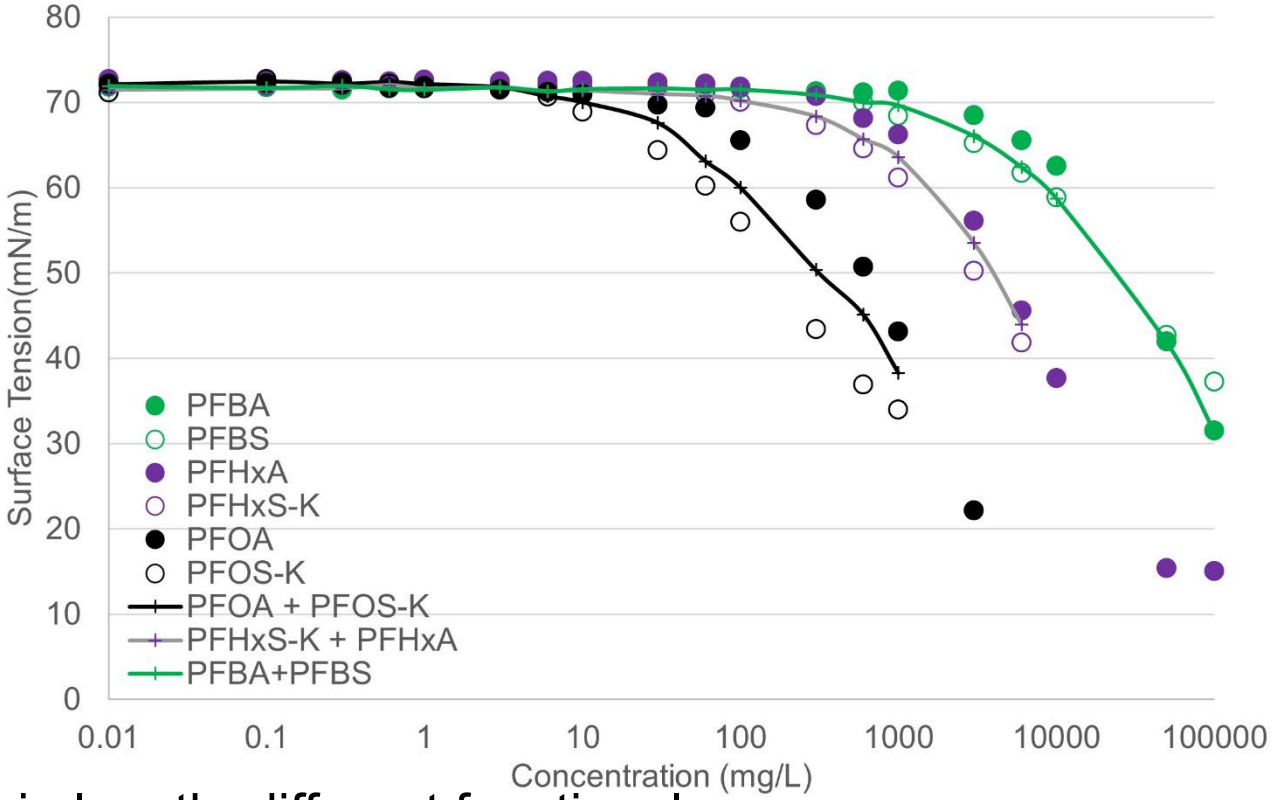



Micelle suspended in water
(above micelle concentration[cmc])




- A sharp decline with increasing concentration.
- Micelle formation in PFHxA and GenX.
- Longer chain < shorter chain; $SO_3^-$ < $COO^-$
- Lowest → PFDA; highest → PFBA
- Highest & Lowest → close to lowest

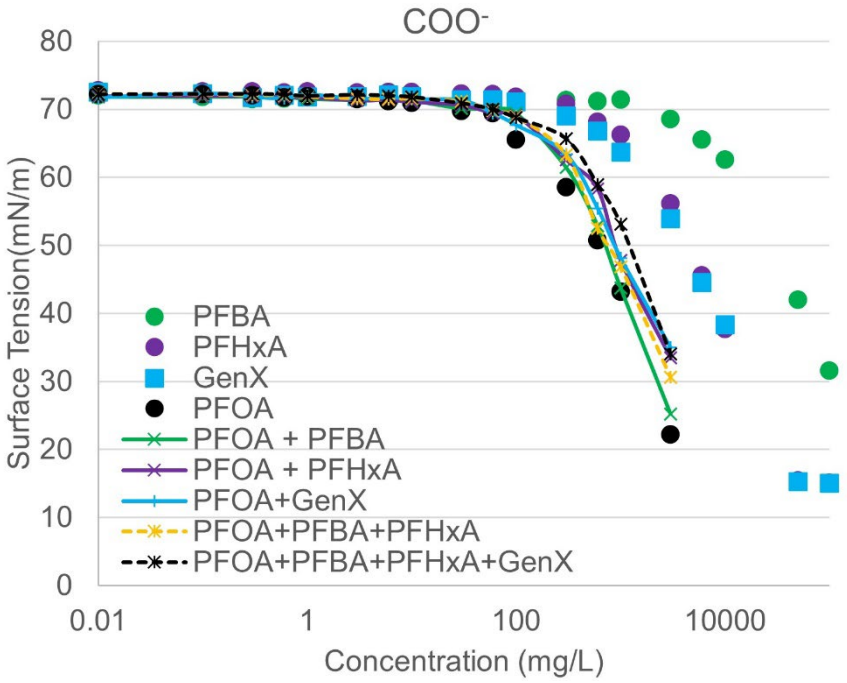
# Results: Surface tension

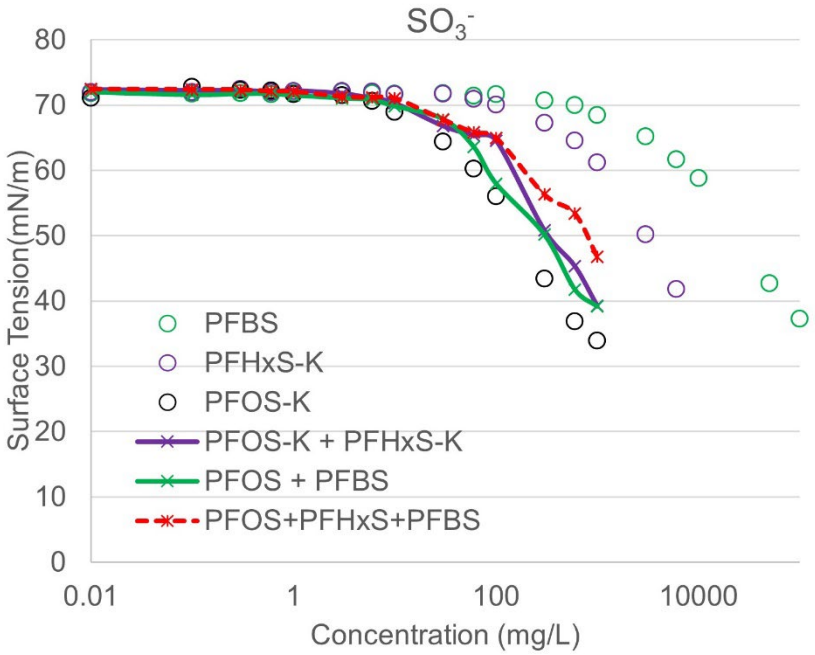



Same C chain length, different functional groups:

- Measurements of mixtures intermediate to individual compounds
- PFBA & PFBS → close to lower individual one

# Results: Surface tension

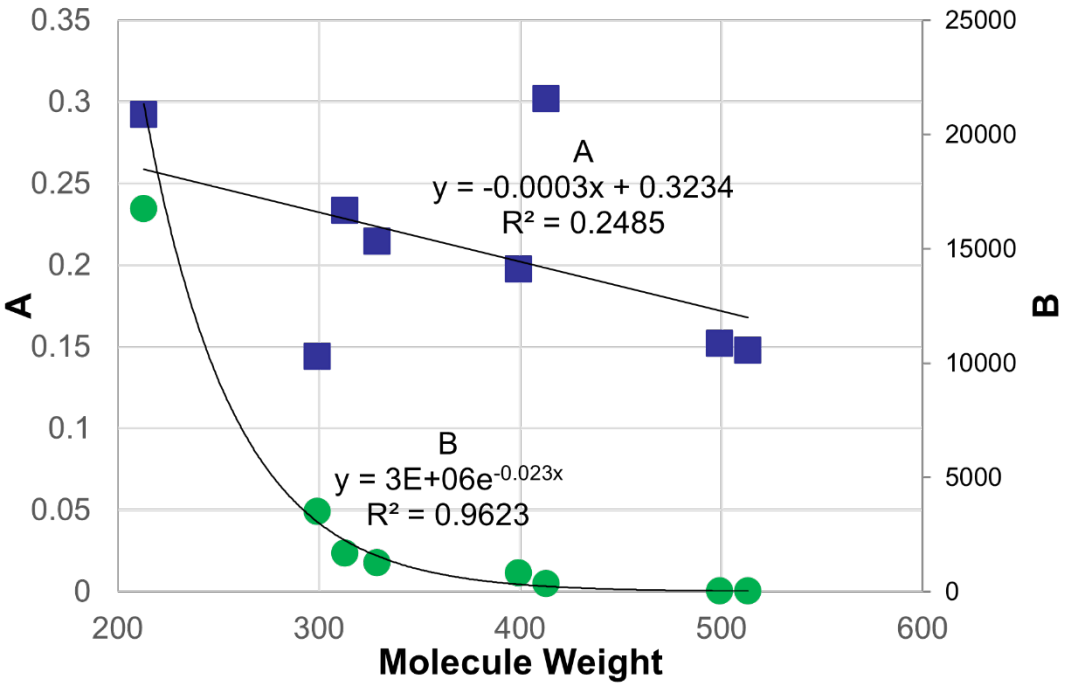



Same functional groups, different C chain length:

- Longest chain (PFOA and PFOS-K) dominates in mixtures
- Binary mixtures: Longest chain are more dominant in mixtures with shortest chain (PFOA + PFBA < PFOA + PFHxA, PFOS-K + PFBS < PFOS-K + PFHxS-K)

# Results: Surface tension



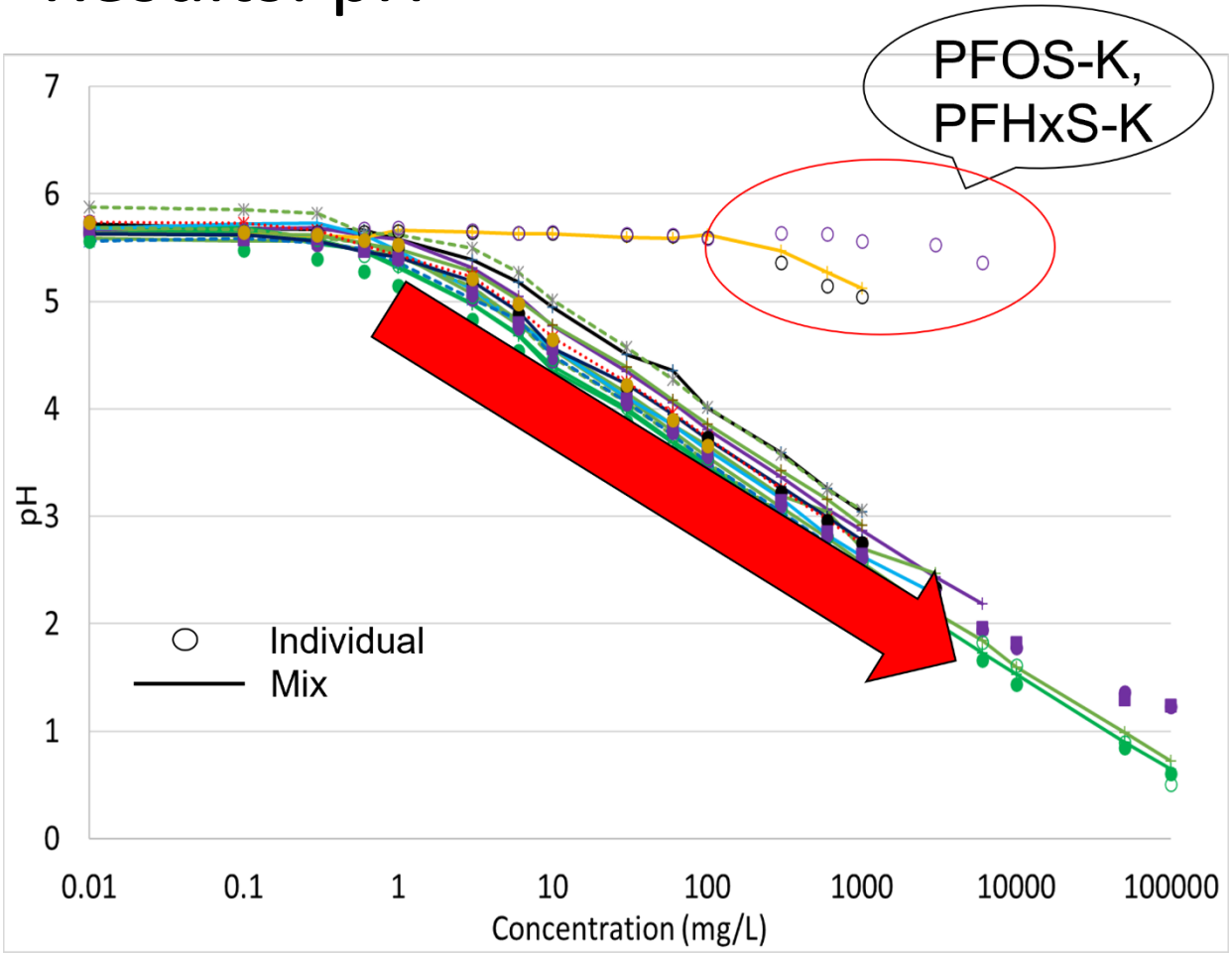

Szyszkowski equation:

$$\gamma = \gamma_0 \left[1 - A\ln\left(1 + \frac{C}{B}\right)\right]$$

- $\gamma$ is surface tension [$MT^{-2}$, mN/m],
- $\gamma_0$ is the solute-free surface tension [$MT^{-2}$, mN/m)],
- C is concentration [$ML^{-3}$, mg/L],
- A and B are model parameters

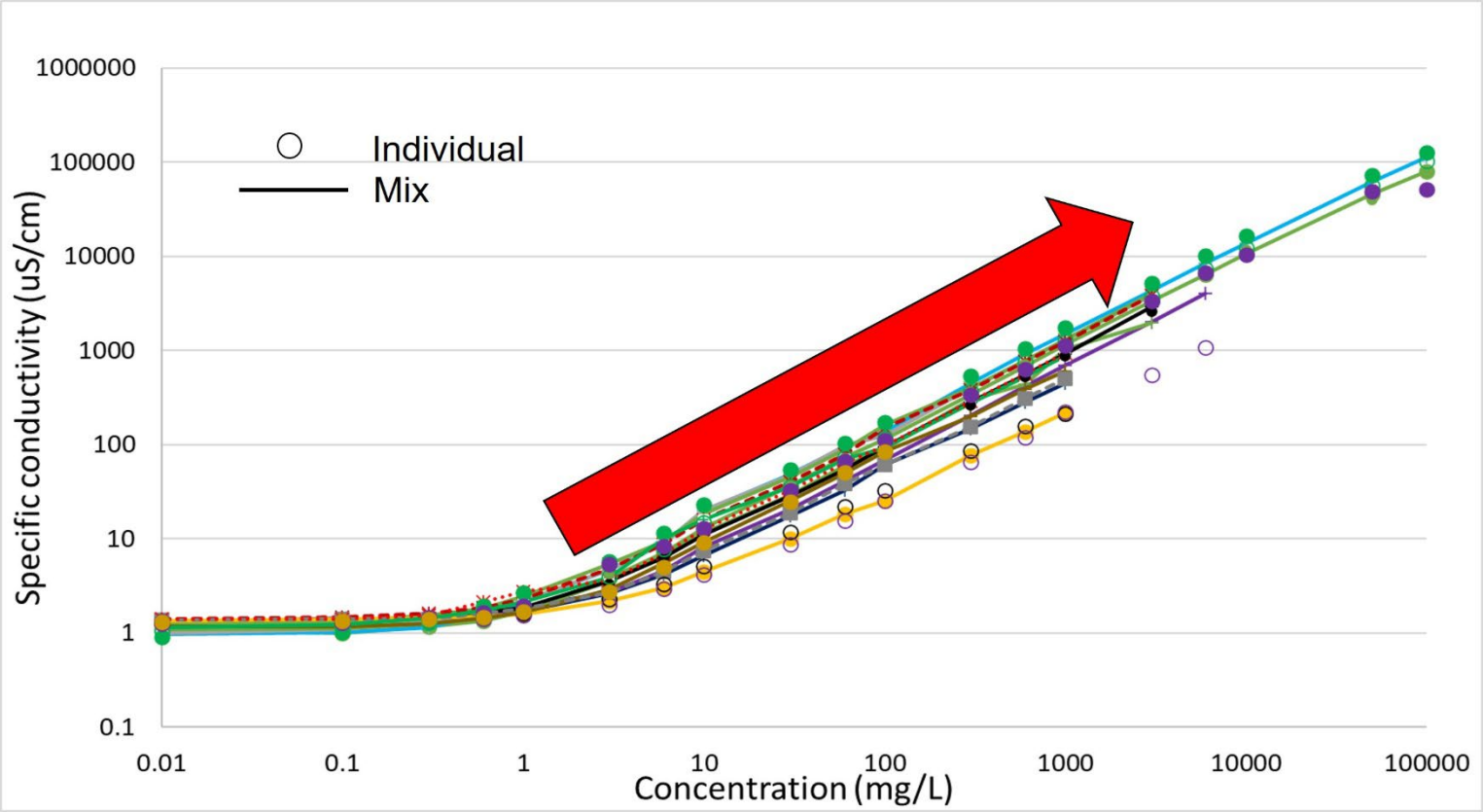
Coefficient of variation of A: ~30%

# Results: pH



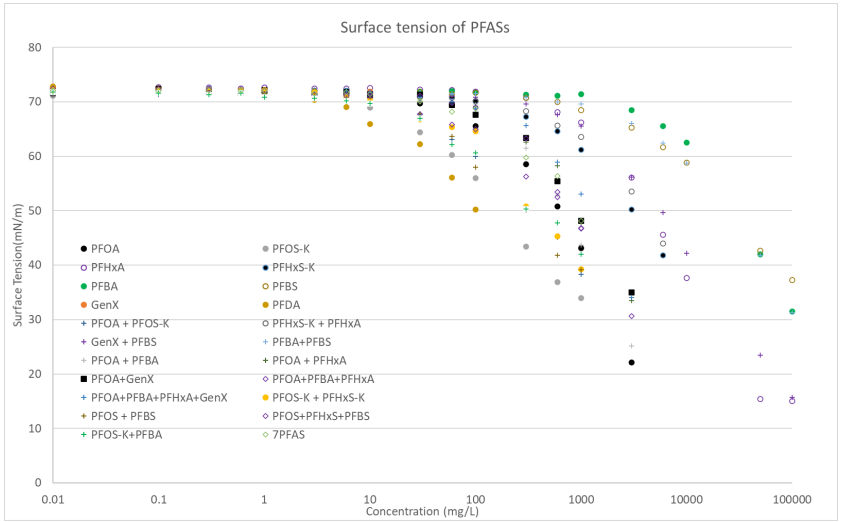

- Highest: PFOS-K and PFHxS-K
- Lowest: PFBA and PFBS
- A sharp decline with increasing concentration

# Results: Specific conductance



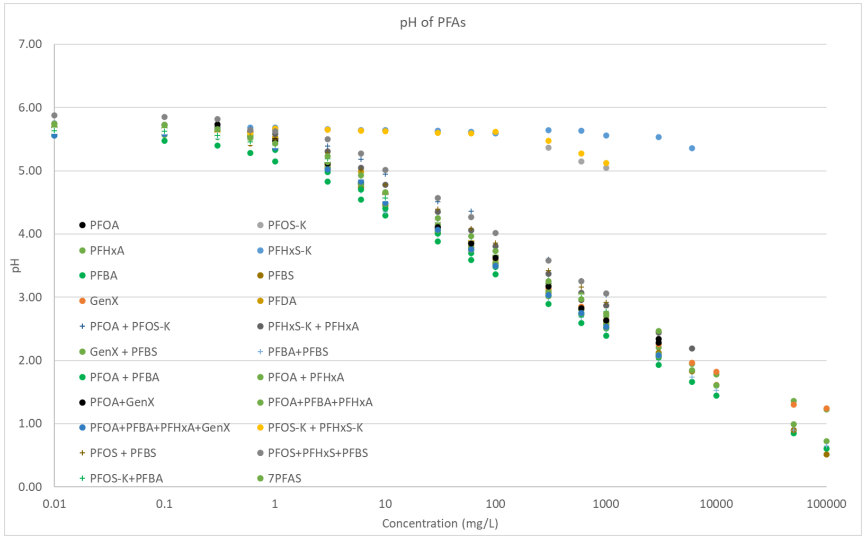

- All have same pattern: exponentially increasing as concentration increased

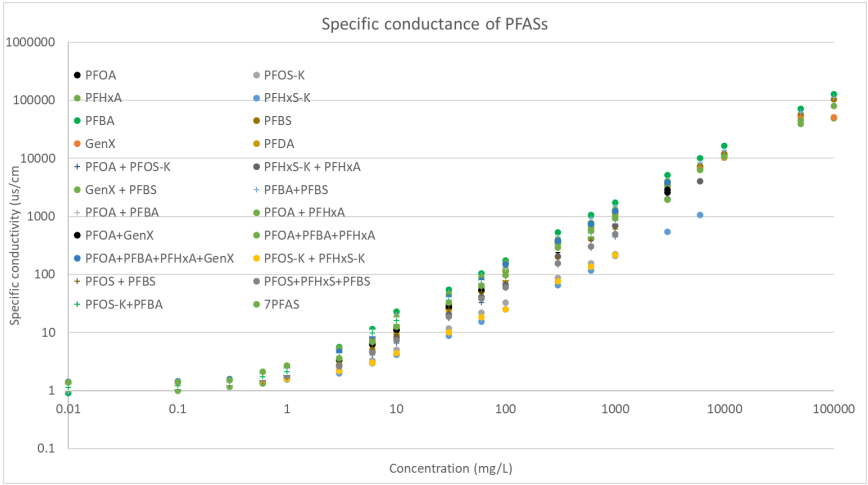
# Screening level tools




- Decreased surface tension
- Decreased pH
- Increased specific conductance

Gives a clue for potential PFAS source zone?



# Conclusions:

- Three stages in surface tension characteristics as a function of concentration: consistent in low concentration, sharply decrease, consistent due to micelle formation.
- C chain and functional group effects: Longer chain < shorter chain; $SO_3^-$ < $COO^-$
- PFAS with longest chain dominates the surface tension behavior.
- PFAS solutions showing low surface tension, low pH, and high specific conductance may indicate a high concentration PFAS source zone.